

## CLAIMS

*what is claimed is:*

1. A method of forming a tungsten nitride layer on a substrate, the method comprising:

5 (a) depositing a gas phase boron-containing agent onto the substrate to form a boron-containing sacrificial layer on the substrate;

(b) exposing the boron-containing sacrificial layer to a tungsten containing precursor to form a tungsten layer;

10 (c) exposing the tungsten layer to a nitriding agent to form a first portion of the tungsten nitride layer; and

(d) performing one or more additional cycles of tungsten nitride deposition to complete formation of the tungsten nitride layer, wherein the additional cycles each comprise contact with reducing agent, tungsten containing precursor, and nitriding agent.

15 2. The method of claim 1, wherein the substrate is a partially fabricated semiconductor device.

20 3. The method of claim 2, wherein the tungsten nitride layer is deposited on at least a portion of exposed dielectric of the partially fabricated semiconductor device.

4. The method of claim 1, wherein the boron-containing agent is a borane.

25 5. The method of claim 1, wherein the boron-containing sacrificial layer is between about 3 and 20 angstroms thick.

6. The method of claim 1, wherein the tungsten containing precursor is  $WF_6$ ,  $WCl_6$ ,  $W(CO)_6$ , or a combination thereof.

30 7. The method of claim 1, wherein the nitriding agent is  $N_2$ ,  $NH_3$ ,  $NF_3$ ,  $N_2H_6$ , or a combination thereof.

8. The method of claim 1, further comprising performing a gas purge after at least one of (a), (b) and (c).

35 9. The method of claim 1, further comprising, after (d), forming a metallic tungsten layer over the tungsten nitride layer.

10. The method of claim 9, wherein the metallic tungsten layer is deposited by CVD.

11. The method of claim 9, wherein the metallic tungsten layer is deposited by a  
5 pulsed nucleation layer process.

12. The method of claim 9, further comprising depositing a copper layer over the metallic tungsten layer.

10 13. The method of claim 12, wherein a first portion of the copper layer is deposited on the metallic tungsten layer using sputtered deposition.

14. The method of claim 13, wherein a second portion of the copper layer is deposited on the first portion of copper by electrolytic plating.

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15. The method of claim 12, wherein the copper layer is a copper seed layer.

16. The method of claim 15, wherein the copper seed layer is deposited from an electroless plating solution.

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17. The method of claim 1, further comprising treating the tungsten layer created in (b) with a hydrogen or argon-hydrogen plasma before exposure to the nitriding agent in (c).

25 18. The method of claim 1, further comprising providing a dopant to the tungsten nitride layer.

19. The method of claim 18, wherein the dopant is at least one of phosphorus, arsenic, antimony, bismuth, boron, aluminum, gallium, indium, nitrogen, and thallium.

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20. The method of claim 1, further comprising, prior to (a), pretreating the substrate by at least one of an annealing operation and a plasma etch.

21. The method of claim 1, wherein the one or more additional cycles of tungsten  
35 nitride deposition comprise exposure to reducing agent that does not include the boron containing agent.

22. The method of claim 21, wherein the reducing agent comprises a silicon hydride.

23. The method of claim 1, further comprising forming a metallic tungsten layer on the tungsten nitride layer to form a gate electrode comprised of the tungsten nitride layer together with the metallic tungsten layer.

24. The method of claim 1, further comprising forming a metallic tungsten layer on the tungsten nitride layer to form a capacitor electrode comprised of the tungsten nitride layer together with the metallic tungsten layer.

25. The method of claim 1, further comprising forming a metallic tungsten plug on the tungsten nitride layer to form a tungsten interconnect, wherein the tungsten nitride layer serves as at least one of an adhesion layer, a diffusion barrier layer, and a nucleation layer for subsequent tungsten deposition.

26. The method of claim 25, further comprising depositing a titanium layer prior to formation of the tungsten nitride layer.

27. The method of claim 1, wherein each of the boron-containing agent, the tungsten-containing precursor, and the nitriding agent are delivered in an inert carrier gas or in a mixture of inert gas with  $N_2$  or  $H_2$ .

28. A method of forming a tungsten nitride layer on a substrate, the method comprising:

- (a) positioning the substrate in a deposition chamber;
- (b) depositing a gas phase reducing agent onto the substrate to form a layer of reducing agent on the substrate;
- (c) exposing the layer of reducing agent to a tungsten containing precursor to form a tungsten layer;
- (d) exposing the tungsten layer to a nitriding agent to form a first portion of the tungsten nitride layer; and
- (e) repeating (b) through (d) for one or more cycles to complete formation of the tungsten nitride layer.

29. The method of claim 28, wherein the reducing agent is a borane.

30. The method of claim 28, wherein the reducing agent is a silane.

31. The method of claim 28, wherein the method takes place sequentially, with (b) performed prior to (c), and (c) performed prior to (d).

32. The method of claim 28, wherein the method takes place sequentially, with (c)  
5 performed prior to (b).

33. The method of claim 28, wherein one or more of the reducing agent, the tungsten containing precursor, and the nitriding agent comprise a different compound when employed to form the first portion of the tungsten nitride layer and when employed in (e).

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34. The method of claim 33, wherein the reducing agent comprises a borane in (b) and comprises a silicon hydride in (e).

35. The method of claim 28, further comprising forming a metallic tungsten layer on  
15 the tungsten nitride layer to form a gate electrode comprised of the tungsten nitride layer together with the metallic tungsten layer.

36. The method of claim 28, further comprising forming a metallic tungsten layer on  
the tungsten nitride layer to form a capacitor electrode comprised of the tungsten nitride  
20 layer together with the metallic tungsten layer.

37. The method of claim 28, further comprising forming a metallic tungsten plug on  
the tungsten nitride layer to form a tungsten interconnect, wherein the tungsten nitride  
layer serves as at least one of an adhesion layer, a barrier layer, and/or a nucleation layer  
25 for subsequent tungsten growth.

38. The method of claim 28, further comprising forming a copper seed layer over the  
tungsten nitride layer, wherein the tungsten nitride layer comprises a diffusion barrier.

39. The method of claim 28, wherein at least one of (b), (c), (d) and (e) occur in a  
30 different station than (a) in a multiple station apparatus.

40. The method of claim 28 further comprising a plasma exposure after (b), (c), (d) or  
any combination thereof.

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41. The method of 40 in which the plasma is an RF plasma containing Ar, N<sub>2</sub>, H<sub>2</sub>,  
NH<sub>3</sub>, or any combination thereof.

42. The method of 40 in which the plasma is remote from the reaction chamber and contains Ar, N<sub>2</sub>, H<sub>2</sub>, NH<sub>3</sub>, or any combination thereof.

5 43. The method of claim 28 in which tungsten nitride deposition is carried out in a multi-station reaction chamber in which

(a) tungsten nitride is deposited at one or more deposition stations in the chamber;

10 (b) pulsed nucleation layer (PNL) tungsten is deposited at zero, one or more stations in the reactor;

(c) CVD tungsten is deposited at zero, one or more stations in the reactor;

(d) the substrate is moved from one deposition station to another such that a layered film of tungsten nitride, PNL-tungsten, and CVD-tungsten is formed; and

15 (e) the layered films of (d) can be combined in any order and for any number of layers.

44. The method of claim 28, wherein the tungsten nitride is deposited in a dedicated tungsten nitride module with one or more deposition stations;

20 wherein the tungsten nitride module contains a wafer preheat station, and a substrate preclean station;

wherein the preclean module provides features for a reactive preclean that makes use of a fluorine based clean chemistry generated by dissociation of a fluorine containing reagent using an inductively coupled plasma; and

25 wherein the wafer preclean station or another station in the tungsten nitride deposition module possesses features for passivating the substrate after substrate precleaning.

45. The method of claim 28, further comprising passivating the substrate by means of one or more of the following: (a) hydrogen exposure; (b) exposure to a remote H/H<sub>2</sub> plasma; (c) exposure to direct H/H<sub>2</sub> or Ar/H/H<sub>2</sub> or a RF plasma; (d) exposure to WF<sub>6</sub>; (e) exposure to H<sub>2</sub> or H/H<sub>2</sub> plasma and NH<sub>3</sub> in series or simultaneously; and (f) exposure to oxygen.

46. The method of claim 28, wherein a module for tungsten nitride deposition is vacuum integrated with a module dedicated for pulsed nucleation of tungsten or CVD of tungsten.

47. A method of forming a tungsten nitride layer on a substrate, the method comprising:

- (a) positioning the substrate in a deposition chamber;
- (b) depositing a one or more layers of pulsed deposition tungsten on the semiconductor wafer;
- (c) depositing one or more layers of pulsed deposition tungsten nitride on the one or more layers of tungsten; and
- (d) optionally repeating (b)-(c) to generate either a bilayer of W-WN or a multi-layered structure of multiple tungsten and tungsten nitride layers.

48. The method of claim 47 in which the bottom layer of the W-WN composite film is a tungsten layer.

49. The method of claim 47 in which the bottom layer of the W-WN composite film is a WN layer.

50. The method of claim 47, wherein the ratio of W and N atoms are present in the W and WN layers in a ratio of approximately 2-to-1, such that stoichiometric  $W_2N$  is formed directly, or indirectly by a heat treatment.